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Dynamically formed inner skin hollow fiber polydimethylsiloxane/polysulfone composite membrane for alcohol permselective pervaporation

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ABSTRACT

This work is concerned with the preparation of alcohol permselective inner skin hollow fiber composite membrane using a dynamic cross-flow coating method. The membranes were successfully prepared by dynamically coating polydimethylsiloxane (PDMS) on the inner surface of the polysulfone (PS) hollow fibers under a pressure-driven process. The strategy of alternating PDMS casting solution direction was firstly explored to ensure the formation of a uniform and defect-free selective layer. Subsequently, the effects of coating time, polymer concentration, and crosslink agent concentration on alcohol permselective performance were investigated. The appropriate conditions were: coating time, 60 min; PDMS concentration, 22.8 wt.%; and TEOS concentration, 1.5 wt.%. Under the given conditions, in the case of pervaporation separation of 8 wt.% ethanol–water mixture (50 °C), the membrane had a separation factor of 6.4 and a permeate flux of 265 g/(m^2 h), respectively. The pervaporation separation behavior of various alcohol/water mixtures with the alcohols being t-butanol, 2-propanol was also investigated. SEM, AFM and contact angle analyses confirmed the formation of selective layer on the inner surface of hollow fibers. Therefore, it indicates that the dynamic cross-flow coating technique is a unique approach to the construction of selective layer on porous hollow fiber substrates, which could emerge as a powerful technique for the preparation of a range of separation membranes.

1. Introduction

In recent years, the exploitation and utilization of new energy have increasingly attached attentions due to global energy crisis issue. Fuel ethanol has widely been recognized as a sort of clean and sustainable energy [1–4]. Currently, about 90% fuel ethanol is produced by biological fermentation method. Generally, the ethanol content could reach 1–15 wt.% in the fermentation broth [5]. The relatively high ethanol concentration resists the fermentation process. Therefore, in situ removal of ethanol from fermentation broth would result in more efficient fermentation. Distillation is traditionally used to recover ethanol from dilute fermentation solution, which has energy and capital cost disadvantages [5]. In recent decades, pervaporation has gained increasing attention for the recovery of ethanol from broth due to its operational simplicity, nontoxicity to microorganism, and economical superiority [6]. Currently, the plate-and-frame is the dominating module configuration employed in pervaporation. In comparison with the plate-and-frame module, the hollow fiber has the advantages such as high-packing density, a self-contained mechanical support, a self-contained vacuum channel and economical superiority [7–11]. Hollow fiber pervaporation membrane includes inner and outer skin modules according to the selective layer location on the inner and outer surface of hollow fibers. In fact, comparing with outer skin module, inner skin membrane possesses its own advantages such as easily protection of the defect-free separation layer, good distribution of feed solution and low resistance in the permeate side [12]. In our laboratory, inner skin hollow fiber composite membrane was prepared by using a dynamic negative pressure layer-by-layer technique. Dynamically formed 1-m long hollow fiber pilot-scale module has been successfully used for pervaporation dehydration [12,13]. However, few studies have dealt with the alcohol permselective inner skin hollow fiber pervaporation membrane.

Dip-coating is one of the classical methods to prepare composite pervaporation membranes. Polymer solution is directly upon the finely porous surface of a supporting membrane forming a very thin film of a polymer [14]. However, in the case of hollow fiber module, it is difficult to obtain inner separation layer using this method. Dynamic formed membrane (DFM) is formed by filtration through a porous support of a dilute solution containing specific membrane forming materials [15–17]. With regard to the dynamically coated

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membrane, the coating layer of was consecutively formed with the coating time onto the support membrane surface in a dynamic manner. DFM may offer some advantages such as abundant membrane material sources and easily formation of separation layer on different support. Therefore, it is regarded as a very promising separation membrane [17,18]. In fact, considerable works have been carried out for the preparation of UF and MF membranes based on DFM [18,19]. However, few works have prepared pervaporation membranes using dynamic formed technology [12,13,16].

Considering the fact that dynamic formed method could potentially be used for the preparation of different membrane module, it was expected that the dynamic coating method could be used to prepare the inner skin hollow fiber membrane for alcohol permselective pervaporation in this work. Polydimethylsiloxane (PDMS), with hydrophobic character, good film-forming properties and outstanding physical and chemical stability, is selected as a typical alcohol permselective polymer. To date, PDMS is still the dominant organic material for alcohol permselective membrane [20]. For example, Jin et al. recently prepared PDMS/ceramic composite membrane for pervaporation separation of ethanol–water by means of depositing PDMS on the outer surface of tubular nonsymmetric ZrO_2/Al_2O_3 porous ceramic support using a dip-coating method [21,22]. Matsuda et al. studied ethanol recovery using a PDMS-coated silicalite plate sheet pervaporation membrane [23,24]. Lai et al. prepared polyimide (PI)/PDMS segmented copolymer membrane followed by thermal dehydration [25]. Cheng and Chang prepared a flat composite membrane by coating thin PDMS layer on polynvinylidene-fluoride (PVDF) supporting layer [26]. Jia et al. reported the zeolite filled PDMS composite membranes. Both PDMS and zeolite filled PDMD selective layers were formed onto polyetherimide (PEI) porous membranes by dip-coating method [27]. Vankelecom et al. mainly investigated the intrusion of PDMS in different porous supports using spectroscopical and gravimetrical methods. They demonstrated that the pretreatment of porous supports had great influences on the resulting composite membrane performances [28]. Obviously, a review of literature revealed that PDMS was commonly used as an alcohol permselective material in flat and tubular composite membrane in previous studies. To our best knowledge, none of works have referred to the inner skin PDMS hollow fiber pervaporation membranes.

In this study, the preparation of PDMS/PS hollow fiber composite membrane for alcohol permselective pervaporation was attempted through dynamically coating PDMS on the inner surface of PS hollow fiber support. To ensure the formation of uniform and defect-free separation layer, the strategy of regularly alternating casting solution direction was explored. As shown in Fig. 1, PDMS casting solution was dynamically filtrated under a transmembrane pressure. After a certain interval, the direction of PDMS solution fed into the lumen side of hollow fibers was regularly alternated and consecutively filtrated. In this way, PDMS was compulsorily coated onto the inner surface of PS hollow fibers. The selective layer was thereby dynamically formed. Except for the coating strategy, the effects of coating method, coating time, PDMS concentration and TEOS concentration were also investigated. The pervaporation separation behavior was studied with ethanol–water, 2-propanol–water and t-butanol–water mixtures. The formation of separation layer on the inner surface of the hollow fibers was further confirmed by using a scanning electron microscopy, an atomic force microscopy and contact angle analyzer.

2. Experimental

2.1. Materials

PDMS with the viscosity of 2550 Pa S was purchased from China Bluestar Chengrand Chemical Co. Ltd. Tetraethyl silicate (TEOS) and ethanol were obtained from Beijing Chemical Company. Dibutyltin dilaurate, n-heptane, tert-butanol (t-butanol) and isopropanol were supplied by Tianjin Fuchen Chemical Reagents Company. In our experiments, all the reagents were analytical grade and used without further purification.

2.2. Hollow fiber support membrane

The hollow fiber support membranes used in this study were produced by the phase inversion method from polysulfone (PS) polymer in our workshop [29]. The inner diameter of each hollow fiber was 1.1 mm. The PS fiber membranes with an effective length of 15 cm were orderly immersed into 25, 50 and 75 wt.% ethanol–water mixtures and then ethanol solvent. The immersion time in each ethanol–water mixture was 3 h. After that, the membranes were taken out and dried under ambient conditions. The fibers were then put into a polymethylmethcrylate tube with a diameter of 1.5 cm. Both ends of the tube were sealed with epoxy resin. After 24 h for the epoxy to get cured, the membrane modules

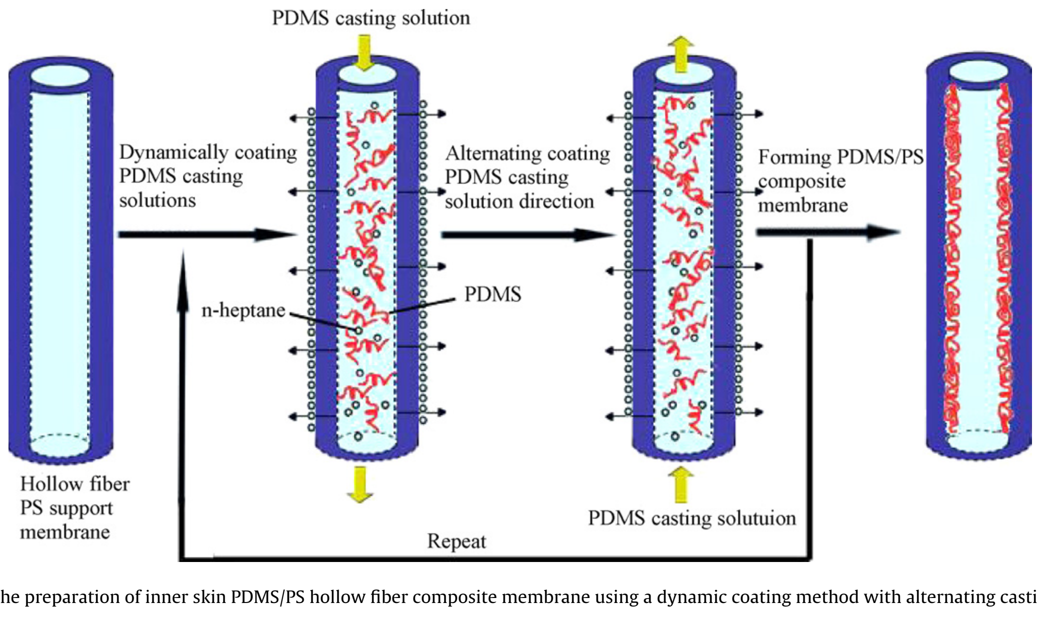

Fig. 1. Principles of the preparation of inner skin PDMS/PS hollow fiber composite membrane using a dynamic coating method with alternating casting solution direction.

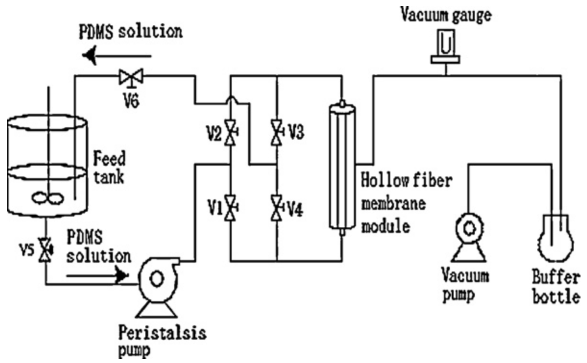

Fig. 2. Experimental apparatus for preparation of inner skin hollow fiber PDMS/PS composite membrane by a dynamic coating method with alternating casting solution direction.

were mounted onto the dynamic filtration system for subsequent coating. The packing density of hollow fiber membrane module was about 180 m^2/m^3.

2.3. Preparation of inner skin hollow fiber PDMS/PS composite membrane by dynamic coating method

PDMS was dissolved in n-heptane to form PDMS solution. After the polymer solutions were stirred at room temperature for 1 h, cross-linking agent TEOS and 0.9 wt.% of catalyst dibutyltin dilaurate were added into polymer solution. The preparation of composite membranes was carried out by using a dynamic negative pressure cross-flow filtration system, which has been shown in Fig. 2. The PDMS solutions were provided into the lumen side of hollow fiber membrane using a peristaltic pump. In this study, in order to form relatively uniform and defect-free separation layer, the strategy of alternating casting solution direction was attempted. As shown in Fig. 2, the direction of PDMS casting solution could be altered by manipulating four valves including V1, V2, V3 and V4. Like a wastewater ultrafiltration system we have previously described [30], when V1 and V3 were opened while V2 and V4 were closed, the casting solution direction was from the bottom to the top. On the other hand, when V2 and V4 were opened while V1 and V3 were closed, the feed direction was from the top to the bottom. Additionally, in order to coat the PDMS on the inner skin surface, a vacuum pump was used to form a negative pressure on the shell side. The experiments were conducted under a negative pressure of 0.09 ± 0.004 MPa. The interval between two alternations of PDMS solution direction was 15 min. After dynamically coating, the membrane module formed was then put in an oven and dried over 24 h at 50 °C. As a control, dynamic dead-end coating was also conducted. In this case, only valve V1 was opened while V2, V3 and V4 were closed.

2.4. Pervaporation separation of alcohol/water mixture

As previously reported [12,13], the pervaporation experiment was conducted using a self-made pervaporation apparatus. The lumen side was used as the feed side while the shell side was used as the permeate side. The alcohol concentration in feed solution was selected as 8 wt.%. The experiments were conducted at a feed temperature of 323 K. The down-stream pressure was about 100 Pa. Each experiment run for PV process was 8 h. The sampling was performed once per hour. The pervaporation performance was measured three times by using three modules with same fabrication and modification conditions, and the average was used as a data point. The permeate vapor was trapped with liquid nitrogen and measured by gas chromatography (GC-14C, SHIMADZU). The permeation flux was determined by measuring the weight of liquid collected in the cold traps during a certain time under steady-state conditions. The separation factor was calculated from the quotient of the weight ratio of alcohol and water in the permeate, Y_{ROH}/Y_{HOH}, and in the feed, X_{ROH}/X_{HOH}:

$$\alpha = \frac{Y_{ROH}/Y_{HOH}}{X_{ROH}/X_{HOH}}$$

2.5. SEM, AFM and contact angle experiments

The inner surface and cross-section of PS hollow fiber support and PDMS/PS composite membrane obtained were observed by SEM (JSM6700F, Japan). All membrane samples were dried under vacuum and fractured in liquid nitrogen. Surface topography was also observed in tapping mode by an atomic force microscopy (AFM) (Pico Scan^{TM} 2500, USA). To observe the inner surface, the hollow fibers were cut longitudinally using a sharp razor blade. A small piece was then placed in-between two clean microscope slides and was made in flat under a slight pressure. Water contact angle measurements were also performed using a contact angle analyzer (DSA 100, Germany).

3. Results and discussion

3.1. Advantage of dynamic coating with alternating casting solution direction

In previous studies on dynamic formed membrane, casting solution was usually provided into hollow fibers along single direction. In this study, dynamic coating with alternating casting solution direction was firstly attempted. The hollow fiber composite membranes formed from different dynamic coating methods were compared. The pervaporation results are shown in Table 1. In comparison with the membrane obtained from dynamic dead-end coating method, the dynamically cross-flow coated membrane exhibited both higher selectivity and permeability. For example, dynamically cross-flow coated membrane had a separation factor of 2.2 and a permeate flux of 3795 g/(m^2 h). As a comparison, these two values obtained from dynamic dead-end coated membrane was only 1.2 and 502 g/(m^2 h). In the experiment, we observed that the portions of the fibers near the entrance could be severely blocked by PDMS strands during the dynamic dead-end coating process. Note that the fibers blocked by PDMS at one entrance end usually led to incompletely coating along the whole fiber. Since pervaporation process is governed by a solution-diffusion mechanism, defects in the selective layer would normally result in lower selectivity. Meanwhile, the fiber blocking would cause the decrease of permeate flux. During dynamic cross-flow coating process, the pressure differential across the support membrane might drive PDMS to aggregate towards the big pores and then in situ seal the defects, which offered a approach to form an integrated selective layer within a relatively short time. Moreover, the blocking phenomena caused by PDMS strands could be alleviated. It was also noted that the strategy of alternating casting solution direction during dynamic coating process resulted in much higher selectivity. The separation factor changed from 2.2 to 3.5 while the flux reduced from 3795 to 2065 g/m^2 h after using alternation strategy. The reason was that PDMS could be much more uniformly coated on both sides of the inner surfaces of PS hollow fiber support. The probability of the defect formation would be highly reduced. Hence, the strategy of regularly alternating casting solution direction could avoid blocking the entrance end of hollow fibers and improve the uniformity of selective layer. In view of the above fact, this method was adopted to prepare alcohol permselective inner skin hollow

Table 1
Comparisons of the composite membranes obtained from different dynamic coating method.

Deposition method	Ethanol concentration in feed (wt.%)	Ethanol concentration in permeate (wt.%)	Total flux (g/m^2 h)	Separation factor (α)
Dynamic dead-end coating	8	9.86	502	1.2
Dynamic cross-flow coating along single direction	8	16.73	3795	2.2
Dynamic cross-flow coating with alternating casting solution direction	8	25.17	2065	3.5

Preparation conditions: composite time: 1 h, PDMS concentration: 9.0 wt.%, TEOS concentration: 0.9 wt.%, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature: 25 °C; pervaporation conditions: feed temperature: 50 °C, pervaporation time 2 h, vacuum pressure: 100 Pa.

Table 2
Comparison of pervaporation performance with literature.

PDMS composite membrane material	Membrane module type	Membrane preparation method	Ethanol concentration in feed solution (wt.%)	Total flux (g/m^2 h)	Separation factor (α)	Reference
PDMS/Ceramic	Tubular	Dip-coating	4.3	19,500	5.7	[22]
PDMS/PVDF	Flat sheet	Dip-coating	10.0	900	31.0	[26]
PDMS/PEI	Flat sheet	Dip-coating	7.0	530	4.4	[27]
PDMS/PI	Flat sheet	Plasma polymerization	6.6	32	6.6	[31]
PDMS/PTFE[a]	Flat sheet	–	6.0	1,530	14.0	[32]
PDMS/PS	Hollow fiber	Dynamical cross-flow casting	8.0	265	6.4	This study[b]

[a] Purchased from Japan Gore-tex, Inc. (Tokyo, Japan).

[b] Preparation conditions: dynamic coating time 1 h, PDMS concentration 22.8 wt.%, TEOS concentration 1.5 wt.%, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C.

fiber composite membrane in the subsequent experiments. Consequently the membrane selectivity could further be improved to 6.4 while the flux was kept at 265 g/m^2 h under the selected appropriate conditions (Table 2). As shown in Table 2, these values were comparative with those obtained from other types of PDMS composite membranes in literatures. Considering the advantages of inner skin hollow fiber pervaporation modules and the difficulties in the preparation of this type of module using dip-coating method, dynamic cross-flow coating with alternating strategy has great potential for further research and applications.

3.2. Effects of dynamic coating time

The effects of dynamic coating time on the pervaporation performance of hollow fiber composite membrane are shown in Fig. 3. Obviously, the selectivity showed a trend of first increase and then decrease. For example, the separation factors obtained from the dynamic coating time of 30 and 60 min were 2.2 and 3.5, respectively. This suggested that the inner surface pores of PS support cannot be completely covered with PDMS within a short time of 30 min. After 60 min coating, a defect-free PDMS selective layer could be formed. However, the separation factor decreased from 3.5 to 2.6 while the total flux increased from 2065 g/(m^2 h) to 7007 g/(m^2 h) when coating time increase to 90 and 120 min. This indicated that excessive coating would not benefit for pervaporation performance. At the beginning of dynamic coating process, n-heptane solvent could pass through the PS hollow fiber support membrane under the pressure-driven process (Fig. 1). As the coating time increased over 60 min, the support membrane pores were almost completely covered by PDMS and in turn a relatively uniform and dense layer was formed on the inner surface. The penetration of n-heptane through the hollow fiber support would become difficult due to the resulting dense layer. Therefore, excessive coating time would lead to the swelling of underlying PDMS layer because of the exceeding contact between PDMS and n-heptane. As a result, the separation factor decreased and the total flux increased after the coating time exceeded 60 min. Therefore, the appropriate coating time was selected as 60 min.

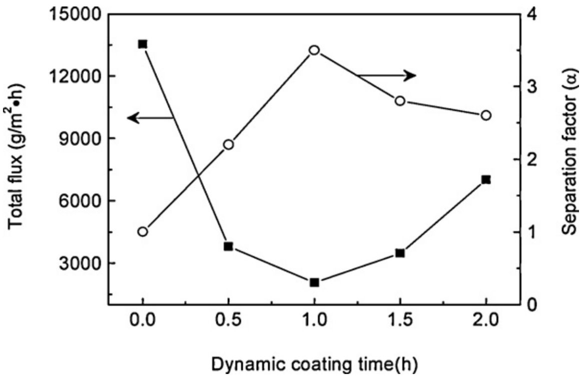

Fig. 3. Effects of dynamic coating time on separation factor and flux (preparation conditions: dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min; pervaporation conditions: feed temperature 50 °C, pervaporation time 2 h, vacuum pressure 100 Pa).

3.3. Effects of PDMS concentration

Fig. 4 shows the effects of PDMS concentration on composite membrane performance. Interestingly, the selectivity firstly increased and then decreased with the increase in PDMS concentration. The separation factor could increase from 3.5 to 5.4 when PDMS concentration varied from 9.0 to 22.8 wt.%. Obviously, the selective layer coated became denser and thicker because the selective layer thickness was usually dependent on the polymer concentration. Furthermore, since the thickness is inversely proportion to total transport resistance, the total permeate flux decreased [21,22]. However, different from dip-coating method, dynamic coating is a unique and promising method. For dynamic coating process, PDMS solution was dynamically filtrated, a relatively diluted solution is required in this method. Otherwise, too high viscosity of casting solution would cause some difficulties for

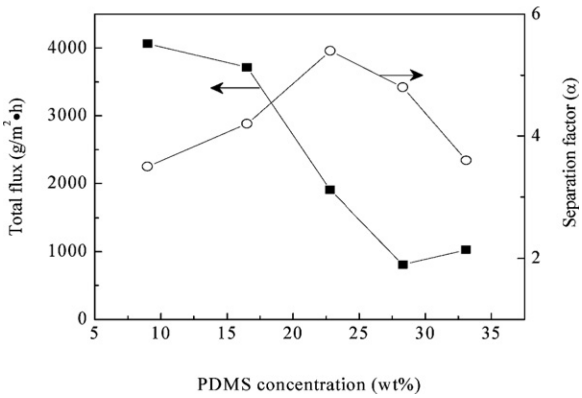

Fig. 4. Effects of PDMS concentration on separation factor and flux (preparation conditions: dynamic coating time 1 h, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min; pervaporation conditions: feed temperature 50 °C, pervaporation time 2 h, vacuum pressure 100 Pa).

dynamic coating. It was observed that the ends of hollow fibers could possibly be blocked in the case of high PDMS concentration, which could result in worse performance. Therefore, it was also noted that the selectivity declined after PDMS concentration increased to 22.8 wt.%.

3.4. *Effects of TEOS concentration*

The cross-linking agent concentration usually plays an important role during the formation of PDMS selective layer. Fig. 5 shows the relationship between membrane performance and TEOS concentration. As shown in Fig. 5, the separation factor increased from 5.4 to 6.4 as the TEOS concentration increased from 0.9 to 1.5 wt.%. It is well known that PDMS could form a three-dimensional network structure owe to the effect of TEOS cross-linking [33]. The cross-linking reaction would cause the decreases of free volume and mobility of polymer segment and in turn the increase of total transport resistance. Therefore, the selectivity increased while the flux decreased after cross-linking treatment. However, excessive TEOS was not beneficial for pervaporation separation. For example, the separation factor dropped to 3.4 when TEOS concentration reached 2.0 wt.%. In pervaporation process, the transport process mainly includes two processes: solution and diffusion of permeating components [34,35]. As we known, water molecular diameter (0.26 nm) is smaller than that of ethanol (0.52 nm) [36]. The diffusion of ethanol molecules would be greatly hindered while the diffusion of water molecules would become relatively easier because excessively increasing TEOS concentration could lead to exceeding dense layer. This in turn resulted in the decrease of separation factor. Moreover, the unreacted TEOS possibly be hydrolyzed and in turn form SiOH due to the contact between TEOS and alcohol aqueous solution during the pervaporation process. The polarity might be higher due to the formation of SiOH, which could also contribute to the decline of selectivity.

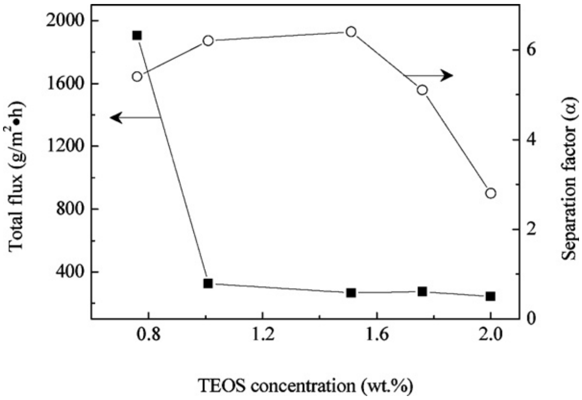

Fig. 5. Effects of TEOS concentration on separation factor and flux (preparation conditions: dynamic coating time 1 h, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min; pervaporation conditions: feed temperature 50 °C, pervaporation time 2 h, vacuum pressure 100 Pa).

Base on the above investigations, the appropriate conditions for dynamically coated PDMS/PS were selected as follows: coating time, 60 min; PDMS concentration, 22.8 wt.%; and TEOS concentration, 1.5 wt.%. Under the given conditions, the membrane obtained had a separation factor of 6.4 and a permeate flux of 265 g/(m^2 h) for pervaporation separation of 8 wt.% ethanol–water mixture (50 °C).

3.5. *Pervaporation separation of different alcohol/water mixture*

Table 3 showed the selectivities and fluxes for the pervaporation different alcohols from aqueous solutions. It was noted from Table 3 that water is entrained by the alcohol through the membrane. The increase in molecular size of alcohol would lead to higher separation performance. For example, in the case of pervaporation separation of t-butanol/water mixture, the separation factor and total flux could reach 9.1 and 814 g/(m^2 h), respectively. This is because that hydrogen bonding is weakened between alcohol and water with increasing number of carbon atoms in the alcohol, which usually resulted in better separation performance. It was also noted that both separation factor and flux obtained from 2-propanol–water mixture were slightly higher than those from t-butanol–water mixture. This reveals an important influence of diffusion on the pervaporation of the branched t-butanol molecule. Vankelecom et al. also reported the similar phenomena using both pure PDMS and zeolite containing PDMS pervaporation membrane [37].

3.6. *SEM, AFM and contact angle analyses*

The inner surfaces and cross-section of hollow fiber membranes before and after dynamically coating PDMS were observed by SEM. The SEM pictures are shown in Fig. 6. In Fig. 6(a), a large number of pores were clearly observed on the inner surface of PS support membrane. In contrast, a new selective layer was formed and covered all the surface pores (Fig. 6(b)). Obvious defects were not found at random selected area. The incorporation of PDMS endowed the membrane with remarkably enhanced density and compactness. The cross-section was characterized at two magnifications of 1000 and 5000. From the cross-sectional SEM pictures (Fig. 6(c)–(f)), it is difficult to distinguish a selective layer on the top of the support membrane. Therefore, the exact thickness data of the top selective layer could not be obtained from the FESEM micrograph. As the above mentioned, one of the advantages with dynamic coating is that the composite selective layer could be formed with a relatively diluted concentration casting solution. Therefore, the selective layer obtained was very thin. Interestingly, the intrusion of PDMS into pores was found in the cross-sectional pictures under dynamic pressure-driven coating process (Fig. 6(d) and (f)), which was beneficial for the improvement of selectivity. The similar phenomena were observed for the cross-section of dynamic layer-by-layer assembled polyelectrolyte multilayer membranes [38,39].

Fig. 7 shows the typical AFM images of the inner surface topography before and after dynamically coating with PDMS solution at two different enlargement multiples. In comparison with Fig. 7(a) and (b), significant changes in surface morphology were observed.

Table 3
Pervaporation performance of inner skin hollow fiber PDMS/PS composite membrane for different alcohol/water feed mixture.

Feed mixture	Alcohol content in feed (wt.%)	Alcohol content in permeate (wt.%)	Total flux (g/m^2 h)	Water partial flux (g/m^2 h)	Alcohol partial flux (g/m^2 h)	Separation factor (α)
8 wt.% ethanol–water	8.0	37.04	576	363	213	6.6
8 wt.% t-butanol–water	8.0	45.64	814	442	372	9.1
8 wt.% 2-propanol–water	8.0	48.11	878	456	422	10.1

The inner surface of PDMS/PS hollow fiber membrane was much rougher than that of PS support membrane. The values of mean roughness (R_a), which were obtained based on $100.0 \times 100.0\,\mu$m scan area (Fig. 7(c) and (d)), increased from 81.8 to 126.5 nm. The increase of R_a might be attributed to the surface enrichment of PDMS and silica growth from TEOS. This further confirmed the formation of selective layer on the inner surface of hollow fiber supports.

The contact angles of PS and PDMS/PS composite membrane are shown in Fig. 8. It was noted that contact angle varied from 72.2° to 88.8° after dynamically coating with PDMS while surface energy decreased from 40.35 to 30 mN/m. Obviously, comparing with PS

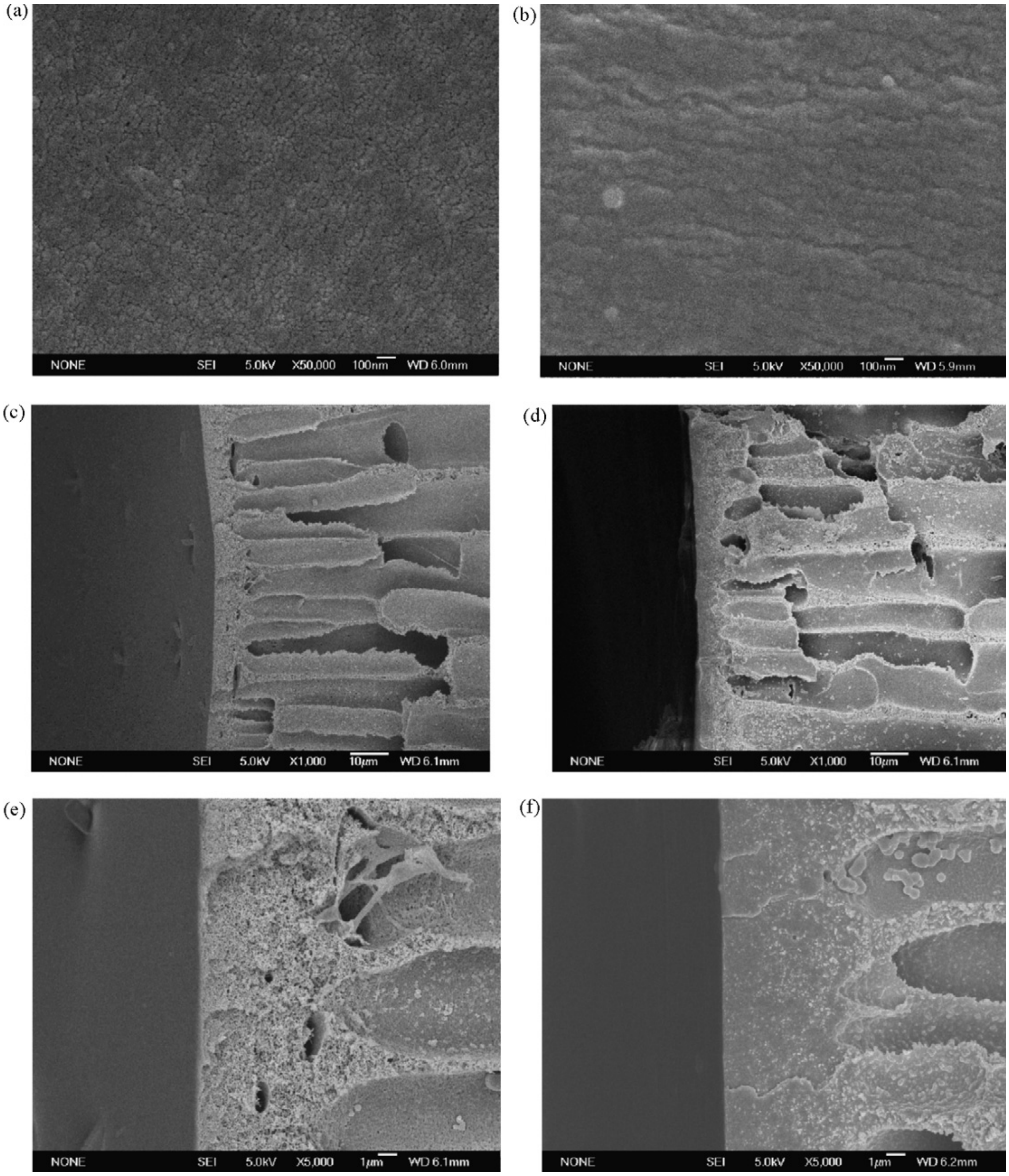

Fig. 6. SEM images of PS pure membrane and PDMS/PS composite membrane (preparation conditions: dynamic coating time 1 h, PDMS concentration 22.8 wt.%, TEOS concentration 1.5 wt.%, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min). (a) Inner surface SEM of PS support membrane (×50.0 k), (b) Inner surface SEM of PDMS/PS composite membrane (×50.0 k), (c) cross-sectional SEM of PS support membrane (×1000), (d) cross-sectional SEM of PDMS/PS composite membrane (×1000). (e) Cross-sectional SEM of PS support membrane (×5000), (f) cross-sectional SEM of PDMS/PS composite membrane (×5000).

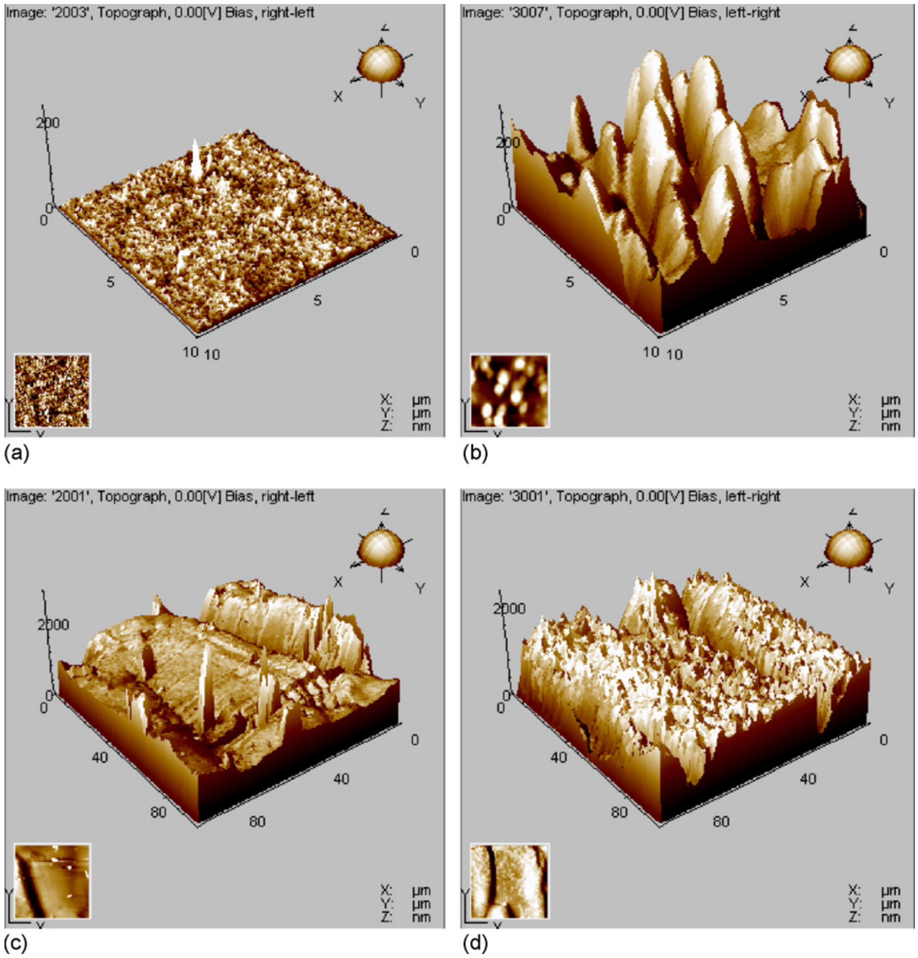

Fig. 7. AFM images of PS pure membrane and PDMS/PS composite membrane inner layer surfaces (preparation conditions: dynamic coating time 1 h, PDMS concentration 22.8 wt.%, TEOS concentration 1.5 wt.%, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min). (a) Inner surface AFM of PS support membrane (10 × 10 µm). (b) Inner surface AFM of PDMS/PS composite membrane (10 × 10 µm). (c) Inner surface AFM of PS support membrane (100 × 100 µm). (d) Inner surface AFM of PDMS/PS composite membrane (100 × 100 µm).

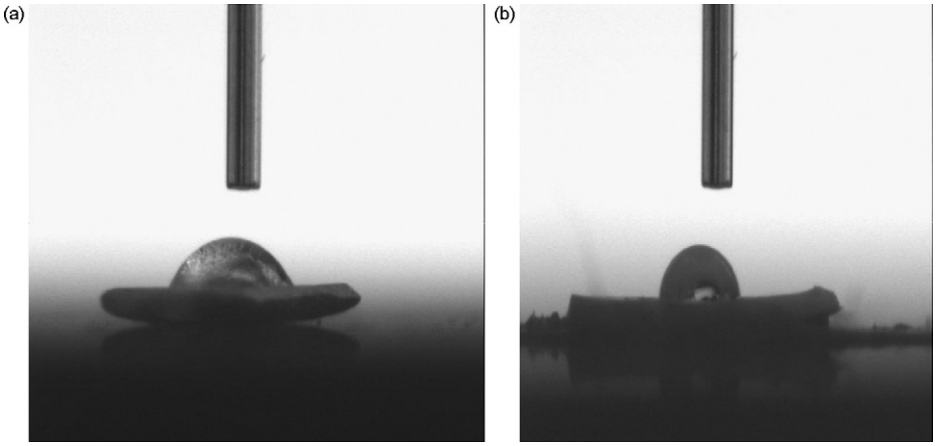

Fig. 8. Contact angle image of inner surfaces of PS support and PDMS/PS composite membranes (preparation conditions: dynamic coating time 1 h, PDMS concentration 22.8 wt.%, TEOS concentration 1.5 wt.%, dynamic negative pressure 0.09 ± 0.004 MPa, preparation temperature 25 °C, interval between two alternations of PDMS solution direction 15 min). (a) PS support membrane and (b) PDMS/PS composite membrane.

virgin membrane, the surface of PDMS/PS composite membrane became more hydrophobic, which would be beneficial for alcohol permselectivity. Linked to the above SEM and AFM experiments, it was confirmed that a dense, rough and hydrophobic selective layer was successfully formed on the inner skin of porous PS hollow fiber support during dynamic coating process.

4. Conclusions

In this study, inner skin hollow fiber PDMS/PS composite membrane was successfully prepared by using a dynamic cross-flow coating method. The effects of different coating process, coating time, PDMS concentration and crosslink agent concentration on membrane performance were intensively investigated. It was found that the strategy of alternating casting solution direction was helpful to construct a uniform and defect-free selective layer and in turn achieved much higher selectivity. The appropriate conditions selected were: PDMS concentration, 22.8 wt.%; crosslink agent TEOS concentration, 1.5 wt.%; and dynamic coating time, 60 min. Under the appropriate conditions, dynamically coated membrane had a separation factor of 6.4 and a permeate flux of 265 g/(m^2 h) (50 °C) for pervaporation of 8 wt.% ethanol–water mixture. The SEM pictures clearly demonstrated that an integrated selective layer was formed. The AFM and contact angle analyses showed that the composite membrane surface became much rougher and more hydrophobic after dynamically coating. In conclusion, the dynamic coating method offers a new approach to fabricate alcohol permselective composite membrane with a defect-free separation layer. Furthermore, it is particular well suited to inner skin hollow fiber module. Expect for alcohol–water mixture, dense PDMS membrane has widely been recognized as a very promising membrane for extraction of volatile organic compounds from aqueous solution and gas separation. Therefore, the inner skin hollow fiber PDMS/PS composite membrane could potentially be used in many separation processes.

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